

Surface Screening Charge and Effective Charge

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The charge on an atom at a metallic surface in an electric field is defined as the field derivative of the force on the atom. This is consistent with definitions of effective charge and screening charge. This charge can be found from the shift in the potential outside the surface when the atoms are moved. This is used to study forces and screening on surface atoms of Ag(001)-c(2 × 2)-Xe as a function of the external field. It is found that at low positive (outward) fields, the Xe with a negative effective charge of $-0.093|e|$ is pushed into the surface. At a field of 2.3 V \AA^{-1} the charge changes sign, and for fields greater than 4.1 V \AA^{-1} the Xe experiences an outward force. Field desorption and the Eigler switch are discussed in terms of these results. [S0031-9007(98)05876-1]

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The force on surface and adsorbate atoms in an applied electric field is important for understanding field evaporation [1], field-induced reconstructions [2], and the movement of adsorbate atoms by STM tips [3,4]. In the limit of low field, the force normal to the surface on atoms of type i is given by

$$F_i = q_i^* \mathcal{E}, \quad (1)$$

where q_i^* is the effective charge on atom i [5–8]. \mathcal{E} is the external electric field above the surface, far enough away from the atoms so that it is uniform—this formula builds in all the local field effects and screening at the surface. The effective charge is also responsible for the change in work function ϕ when atoms of type i are displaced [7,8]:

$$\frac{\partial \phi}{\partial z_i} = -\frac{4\pi q_i^*}{\mathcal{A}_i}. \quad (2)$$

Here z_i is the displacement of the atoms perpendicular to the surface, and \mathcal{A}_i is the area per atom i . The surface effective charge is already familiar to us from the theory of the interaction of probes such as electron energy-loss spectroscopy and infrared with surface vibrations [6], and it is the same as the Born effective charge in polar solids in which there is much current interest [9,10]. In this Letter we shall generalize these ideas to calculate the force on an atom at a metallic surface in an electric field of arbitrary strength. This will allow us to determine not only the effective charge, but also to assign the screening charge to individual atoms.

We use an extension of the classical argument for finding the force on the plate of a parallel plate capacitor—one plate consists of the surface under consideration, and the other is an arbitrary electrode. The potential of the electrode is initially V relative to our surface, which is maintained at constant potential, and the two are discon-

nected. On taking charge dq from the electrode to the surface the energy change of the system is dU , with

$$V = -\frac{\partial U}{\partial q}. \quad (3)$$

If we now move the atoms of type i by dz_i , the potential across the capacitor changes (Fig. 1), in just the same way that the work function changes in the zero-field case. From Eq. (3) we have

$$\frac{\partial V}{\partial z_i} = -\frac{\partial^2 U}{\partial q \partial z_i}. \quad (4)$$

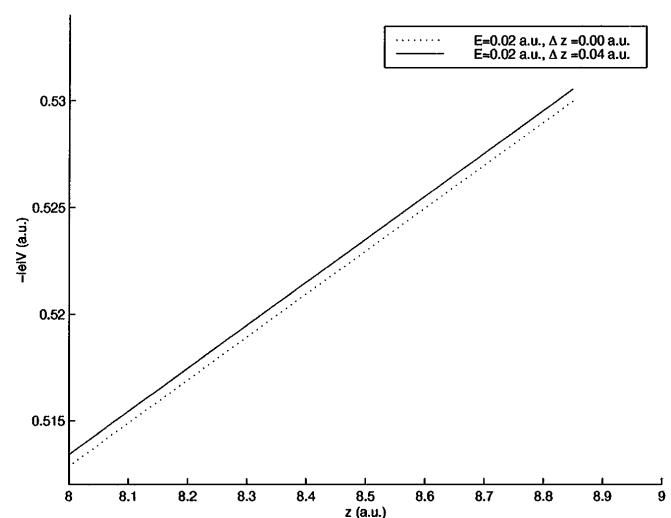


FIG. 1. Shift in electron potential energy outside the surface in an electric field of $+0.02 \text{ a.u.}$, on displacing Xe atoms by 0.04 a.u. into the vacuum. The undisplaced Xe atoms are at $+2.754 \text{ a.u.}$

But $-\partial U/\partial z_i$ is the total force on the atoms of type i , so Eq. (4) becomes

$$\frac{\partial V}{\partial z_i} = N_i \frac{\partial F_i}{\partial q}, \quad (5)$$

where F_i is the force on each atom of type i , and there are N_i such atoms on the surface. Replacing dq by the change in the electric field $d\mathcal{E}$ between the plates we obtain a relationship between $\partial F_i/\partial \mathcal{E}$ and $\partial V/\partial z_i$:

$$\mathcal{Q}_i \equiv \frac{\partial F_i}{\partial \mathcal{E}} = \frac{\mathcal{A}_i}{4\pi} \frac{\partial V}{\partial z_i}. \quad (6)$$

We define $\partial F_i/\partial \mathcal{E}$ as the charge \mathcal{Q}_i on atoms i , and we can then determine it from the right-hand side of Eq. (6). [The difference in sign between Eqs. (6) and (2) arises because V is the electrostatic potential, whereas ϕ is the electron potential energy.] The right-hand side of this expression is easy to evaluate in an electronic structure calculation in the presence of an applied field—we simply have to move the atoms of type i and see how much the potential in the vacuum shifts.

\mathcal{Q}_i is also related to the shift of the center of gravity of the screening charge with atomic displacement. The center of gravity z_0 is the electrostatic origin of the electric field [11,12], which means that

$$\frac{\partial V}{\partial z_i} = \mathcal{E} \frac{\partial z_0}{\partial z_i}. \quad (7)$$

But \mathcal{E} is related to the total screening charge \mathcal{Q} per surface unit cell area \mathcal{A} by

$$\mathcal{E} = \frac{4\pi \mathcal{Q}}{\mathcal{A}}, \quad (8)$$

so from Eq. (6),

$$\mathcal{Q}_i = \frac{\mathcal{A}_i \mathcal{Q}}{\mathcal{A}} \frac{\partial z_0}{\partial z_i}. \quad (9)$$

Now $\mathcal{A}_i/\mathcal{A} = 1/\mathcal{N}_i$, where \mathcal{N}_i is the number of atoms of type i per unit cell, so the charge associated with these atoms is given by

$$\mathcal{Q}_i = \frac{\mathcal{Q}}{\mathcal{N}_i} \frac{\partial z_0}{\partial z_i}. \quad (10)$$

This is an obvious way to divide the charge on the surface between the different atoms, and we conclude that Eq. (6) is a natural and unambiguous definition of \mathcal{Q}_i .

By moving all the surface atoms through dz we simply shift the total screening charge; hence,

$$\sum_i \frac{\partial z_0}{\partial z_i} = 1. \quad (11)$$

So we have the sum rule

$$\sum_i \mathcal{N}_i \mathcal{Q}_i = \mathcal{Q}, \quad (12)$$

and the charge on all the atoms adds up to the total screening charge. If we separate \mathcal{Q}_i into the zero-field

effective charge q_i^* ; plus a term linear in the external field,

$$\mathcal{Q}_i = q_i^* + \alpha_i \mathcal{E}, \quad (13)$$

we see from Eq. (6) that the force on atoms of type i in the field is given by

$$F_i = q_i^* \mathcal{E} + \frac{1}{2} \alpha_i \mathcal{E}^2. \quad (14)$$

The factor of $1/2$ is familiar to us from the force on a capacitor plate. In these expressions for the force, we have implicitly assumed that the atoms have not been allowed to relax from their zero-field positions; what actually happens is that the atoms move in the field so that this electrostatic force is balanced by the interatomic forces, in this way distributing the force as a stress throughout the system.

To show how these ideas can give useful information about bonding and screening, we consider Ag(001)- $c(2 \times 2)$ -Xe, with the Xe atoms adsorbed in atop sites. We have performed self-consistent electronic structure calculations for this system, using the embedding method [13] to include the semi-infinite substrate and treating the top two layers of atoms explicitly. We calculate the charges \mathcal{Q}_i for a range of applied electric fields from Eq. (6), by moving the atoms through small displacements (typically 0.02 a.u.) and calculating the change in electrostatic potential outside the surface. Our results are shown in Table I, and first we note that for all the fields the sum of charges \mathcal{Q}_i is very close to the total screening charge \mathcal{Q} calculated from Eq. (8)—the sum rule (12) is well satisfied. The slight discrepancies are due to the fact that the screening is confined to the top two layers of atoms in our calculation.

In the limit of zero field, we find that Xe has a small negative effective charge, $q_{\text{Xe}}^* = -0.093|e|$, which is largely counterbalanced by a positive effective charge on the underlying Ag atoms. The sign of the effective charge agrees with field emission experiments, which show that a positive field (in our convention, one which corresponds to positive screening charge at the surface) pushes inert gas atoms towards the surface [14].

The negative effective charge on the Xe can be understood in terms of the dipole moment of adsorbed rare gas atoms and its variation with distance [15]. Adsorbed Xe

TABLE I. Charge on atoms at Ag(001)- $c(2 \times 2)$ -Xe, for different electric fields. The Xe atoms are atop Ag(1). The last row shows the total screening charge per surface unit cell calculated from Eq. (8). Charges are in units of $|e|$, and fields in atomic units; a positive field is directed out of the surface.

	$\mathcal{E} = 0$	+0.005	+0.01	+0.02
Xe	-0.093	-0.089	-0.084	-0.069
Ag(1)	+0.086	+0.099	+0.115	+0.136
Ag(2)	+0.002	+0.008	+0.016	+0.031
\mathcal{Q}	0	+0.024	+0.048	+0.097

has a dipole moment pointing out of the surface (positive charge outside, negative charge inside), as is shown by the decrease in work function compared with the clean surface [16]. The physical origin of the positive dipole moment lies in the fact that the vacuum side is less attractive to electrons on the Xe atoms than the metal side, where the exchange-correlation potential is more attractive [17]. Now a van der Waals treatment gives a dipole moment varying as $(z_{\text{Xe}} - z_{\text{vdW}})^{-4}$ [18], where z_{vdW} is the position of the van der Waals plane, so as z_{Xe} increases and the Xe atoms are moved away from the surface, the dipole moment decreases. The work function increases, and this corresponds to a negative effective charge on the Xe atoms. This approach gives

$$q_{\text{Xe}}^* \approx \frac{\mathcal{A}_i}{\pi} \frac{\Delta\phi}{(z_{\text{Xe}} - z_{\text{vdW}})}, \quad (15)$$

where $\Delta\phi$ is the change in work function due to Xe adsorption. Taking $(z_{\text{Xe}} - z_{\text{vdW}}) = 4.2$ a.u., $\Delta\phi = -0.46$ eV, and $\mathcal{A}_i = 60.7$ a.u., we then obtain an effective charge of $-0.08|e|$, in excellent agreement with our first-principles calculation. However, this is not the whole story, as a tight-binding calculation of Xe on Al shows some chemisorption, with real charge transfer of about $-0.1|e|$ to the Xe [19]. Whatever the origin of the effective charge of $-0.093|e|$ on the Xe, it is this charge which determines the force in the low field limit.

As the electric field is turned on, the charge on the Xe atoms becomes slightly less negative, whereas there is a much bigger increase in positive charge on the Ag atoms, particularly Ag(1)—the Ag atom directly underneath the Xe. These results mean that the screening charge is mostly situated on the surface Ag atoms, in agreement with our expectations. What is surprising is that Ag(1) is responding twice as much to the electric field as Ag(2), and there are several possible explanations. First, the Xe lowers the Ag work function, and if this is considered as a local effect we would expect that the valence wave functions on the Ag atoms under the Xe should penetrate deeper into the vacuum [20] and hence respond more strongly to external fields. Second, it may be a local field effect with enhancement of the field under the Xe atoms.

The results for the charge on the Xe shown in Table I, extended to larger electric fields up to $\mathcal{E} = 0.06$ a.u., can be fitted by the formula

$$Q_{\text{Xe}} = -0.097 + 1.165\mathcal{E} + 23.147\mathcal{E}^2 \quad (\text{a.u.}) \quad (16)$$

At a field of 0.044 a.u. (2.3 V \AA^{-1}), the field-induced charge cancels the effective charge, and the charge on the Xe atoms changes sign. The force on the Xe is given by integrating Eq. (16) with respect to \mathcal{E} [Eq. (6)]:

$$F_{\text{Xe}} = -0.097\mathcal{E} + 0.583\mathcal{E}^2 + 7.715\mathcal{E}^3 \quad (\text{a.u.}) \quad (17)$$

In a positive electric field, the Xe atom feels a force towards the surface at low fields. The force towards the

surface initially increases linearly with increasing field, but then decreases, going through zero at $\mathcal{E} = 0.08$ a.u. (4.1 V \AA^{-1}) and directed away from the surface for larger fields. We emphasise that this is the total force on the Xe atoms maintained at the original position, and it takes into account all the field-induced bonding and charging [21], and local field enhancement effects. The change in sign of the force at large fields agrees with cluster calculations of adsorbed rare gas atoms by Nath *et al.* [22]. The rapid variation of F_{Xe} at large \mathcal{E} means that a field somewhat greater than 4.1 V \AA^{-1} will overcome the van der Waals and other bonding forces and remove Xe atoms from the Ag(001) surface. In fact, this certainly overestimates the field needed for field desorption—it does not take account of the nonadiabatic transition to ionized Xe.

The fields necessary for field desorption are much greater than those involved in the manipulation of surface Xe atoms by the STM. In the Eigler switch [23], in which a positively biased tip pulls a Xe atom from the surface and the reverse bias switches it back, typical parameters are a tip bias of +0.8 V with the tip about 4 Å above the surface. This corresponds to an electric field \mathcal{E} of -0.004 a.u. (in our sign convention), so from Eq. (16) we see that Q_{Xe} is essentially the effective charge. This field pulls the Xe towards the tip with a force of 4×10^{-4} a.u., 20 meV \AA^{-1} , much smaller than the force needed to pull a Xe atom directly off the surface (from potential energy curves this is $100\text{--}150 \text{ meV \AA}^{-1}$ [24,25]). As shown by de Andres *et al.* [4] and Walkup *et al.* [15], the importance of the force on the effective charge is that it produces a bias-dependent shift of the potential well of the Xe adsorbed on the tip relative to the well for adsorption on the surface, facilitating the Xe atom jumps.

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- [1] H. J. Kreuzer and R. L. C. Wang, *Philos. Mag. B* **69**, 945 (1994).
 - [2] O. M. Magnussen, J. Wiechers, and R. J. Behm, *Surf. Sci.* **289**, 139 (1993).
 - [3] D. M. Eigler and E. K. Schweizer, *Nature (London)* **344**, 324 (1990).
 - [4] P. L. de Andres, F. Flores, J. R. Cerdá, and P. M. Echenique, *J. Phys. Condens. Matter* **5**, A411 (1993).
 - [5] S. E. Trullinger and S. L. Cunningham, *Phys. Rev. B* **8**, 2622 (1973).
 - [6] D. L. Mills, *Prog. Surf. Sci.* **8**, 143 (1977).
 - [7] D. R. Hamann, *J. Electron Spectrosc.* **44**, 1 (1987).
 - [8] E. A. Colbourn and J. E. Inglesfield, *Phys. Rev. Lett.* **66**, 2006 (1991).
 - [9] R. D. King-Smith and D. Vanderbilt, *Phys. Rev. B* **47**, 1651 (1993).
 - [10] M. Posternak, A. Baldereschi, H. Krakauer, and R. Resta, *Phys. Rev. B* **55**, R15983 (1997).
 - [11] N. D. Lang and W. Kohn, *Phys. Rev. B* **7**, 3541 (1973).

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- [12] G.C. Aers and J.E. Inglesfield, *Surf. Sci.* **217**, 367 (1989).
- [13] J.E. Inglesfield and G.A. Benesh, *Phys. Rev. B* **37**, 6682 (1988).
- [14] N. Ernst, W. Drachsel, Y. Li, J.H. Block, and H.J. Kreuzer, *Phys. Rev. Lett.* **57**, 2686 (1986).
- [15] R.E. Walkup, D.M. News, and Ph. Avouris, *Phys. Rev. B* **48**, 1858 (1993).
- [16] W.R. Merry, R.F. Jordan, D.F. Padowitz, and C.B. Harris, *Surf. Sci.* **295**, 393 (1993).
- [17] N.D. Lang, *Phys. Rev. Lett.* **46**, 842 (1981).
- [18] E. Zaremba and W. Kohn, *Phys. Rev. B* **13**, 2270 (1976).
- [19] R. Pérez, F.J. García-Vidal, P.L. de Andrés, and F. Flores, *Surf. Sci.* **307–309**, 704 (1994).
- [20] D.M. Eigler, P.S. Weiss, E.K. Schweizer, and N.D. Lang, *Phys. Rev. Lett.* **66**, 118 (1991).
- [21] R.L.C. Wang, H.J. Kreuzer, and R.G. Forbes, *Surf. Sci.* **350**, 183 (1996).
- [22] K. Nath, H.J. Kreuzer, and A.B. Anderson, *Surf. Sci.* **176**, 261 (1986).
- [23] D.M. Eigler, C.P. Lutz, and W.F. Rudge, *Nature (London)* **352**, 600 (1991).
- [24] X. Bouju, C. Joachim, C. Girard, and P. Sautet, *Phys. Rev. B* **47**, 7454 (1993).
- [25] N. Mingo, L. Jurczyszyn, F.J. Garcia-Vidal, R. Saiz-Pardo, P.L. de Andres, F. Flores, S.Y. Wu, and W. More, *Phys. Rev. B* **54**, 2225 (1996).